From supramolecular sheets to fibers and back: establishing the critical parameters that govern the morphology of pyrene-based self-assembled materials

Mykhailo Vybornyi, Robert Häner*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3 Bern, CH-3012, Switzerland.

Email: mykhailo.vybornyi@dcb.unibe.ch

The precise arraying of functional entities in morphologically well-defined shapes remains one of the key challenges in the processing of organic molecules[1]. Among various π-conjugated species, pyrene exhibits a set of unique properties, which make it an attractive compound for the utilization in materials science[2]. In this contribution we report on properties of self-assembled structures prepared from amphiphilic pyrene trimers (**Py_3**) consisting of phosphodiester-linked pyrenes. Depending on the geometry of a pyrene core substitution (1.6-, 1.8-, or 2.7- type, see Scheme), the thermally-controlled self-assembly allows the preparation of supramolecular architectures of different morphologies in a bottom-up approach: two-dimensional (2D) nanosheets[3] are formed in case of 1.6- and 2.7-substitution[4] whereas one-dimensional (1D) fibers are built from 1.8- substituted isomers. The morphologies of the assemblies are established by AFM and TEM, and the results are further correlated with spectroscopic and scattering data. Two-dimensional assemblies consist of an inner layer of hydrophobic pyrenes, sandwiched between a net of phosphates. Due to the repulsion of the negative charges, the 2D assemblies exist mostly as free-standing sheets. An internal alignment of pyrenes leads to strong exciton coupling with an unprecedented observation (simultaneous development of J- and H-bands from two different electronic transitions). Despite the similarity in spectroscopic properties, the structural parameters of the 2D aggregates drastically depend on the preparation procedure. Under certain conditions extra-large sheets (thickness of 2 nm, aspect ratio area/thickness ~10^7) in aqueous solution are formed[4B]. Finally, one-dimensional assemblies are formed as micrometer-long and nanometer-thick fibers. Both, planar and linear structures are intriguing objects for the creation of conductive nanowires that may find interest for applications in supramolecular electronics.

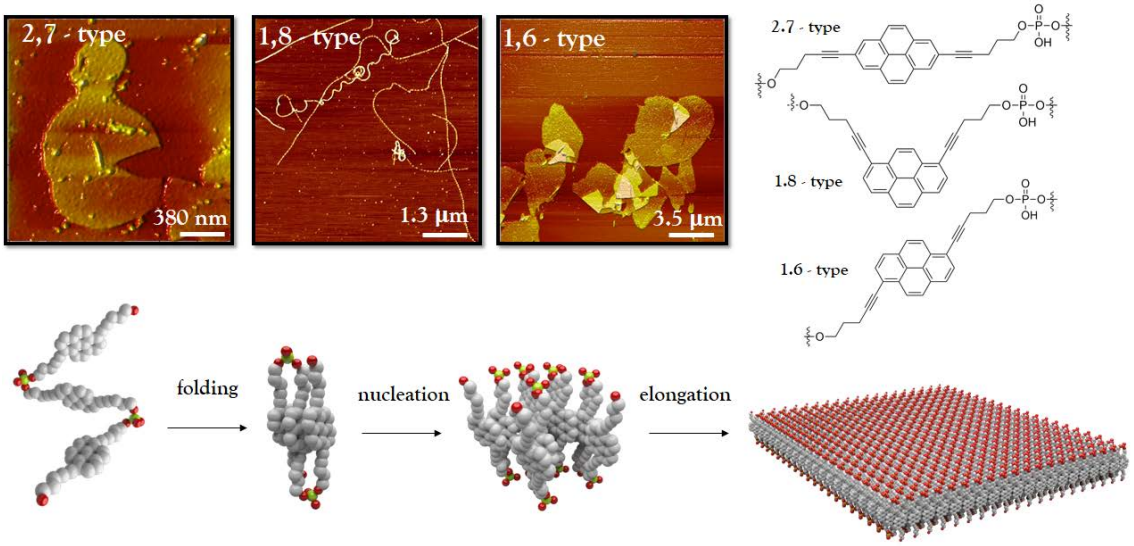

Figure 1. AFM images of the supramolecular polymers (top) and an illustration of the supramolecular polymerization process via a cooperative mechanism (bottom).

References

[1] Aida, T.; Meijer, E. W.; Stupp, S. I. *Science* **2012**, *335*, 813.
[2] Figueira-Duarte, T. M.; Müllen, K. *Chem. Rev.* **2011**, *111*, 7260
[3] Sakamoto, J.; van Heijst, J.; Lukin, O.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **2009**, 48, 1030

[4] A) Vybornyi, M.; Rudnev, A. V; Langenegger, S. M.; Wandlowski, T.; Calzaferri, G.; Häner, R. *Angew. Chem., Int. Ed.* **2013**, *52*, 11488. B) Vybornyi, M.; Rudnev, A. V; Häner, R. *Chem. Mater.***2015**, 27, 1426.